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A Novel *N*-Halamine Monomer for Preparing Biocidal Polyurethane Coatings

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A novel *N*-halamine monomer has been prepared which can be copolymerized with a commercial waterborne acrylic polyol and a commercial isocyanate to produce a polyurethane coating which can be applied to a broad variety of surfaces. After curing, the coating can be chlorinated with a source of free chlorine, such as bleach, to render it biocidal. Once the coating loses its chlorine loading, and hence its biocidal activity, regeneration is possible by further exposure to free chlorine. In one experimental observation a coating on a wall has retained its biocidal activity for more than six months. The biocidal coating should have many applications, including in medical facilities, in food preparation areas, in prevention of biofouling in aqueous and humid environments, etc.

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A novel *N*-halamine monomer for preparing biocidal polyurethane coatings*

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Summaries

A novel *N*-halamine monomer for preparing biocidal polyurethane coatings

A novel *N*-halamine monomer has been prepared which can be copolymerized with a commercial waterborne acrylic polyol and a commercial isocyanate to produce a polyurethane coating which can be applied to a broad variety of surfaces. After curing, the coating can be chlorinated with a source of free chlorine, such as bleach, to render it biocidal. Once the coating loses its chlorine loading, and hence its biocidal activity, regeneration is possible by further exposure to free chlorine. In one experimental observation a coating on a wall has retained its biocidal activity for more than six months. The biocidal coating should have many applications, including in medical facilities, in food preparation areas, in prevention of biofouling in aqueous and humid environments, etc.

Key Words: Biocides, Biofilm Prevention, *N*-Halamines, Paint, Polyurethanes

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INTRODUCTION

Work at Auburn University since 1980 has focused on the development of novel biocidal *N*-halamine derivatives.[1] Water-soluble, cyclic *N*-halamine derivatives such as 1,3-dihalo-5,5-dimethylhydantoin and halogenated isocyanurates (*e.g.*, Trichlor and Dichlor) have been employed as biocides for industrial and recreational water uses for many years, but the water-soluble *N*-halamine compounds produced at Auburn University (oxazolidinones and imidazolidinones) are unique because of their long-term stabilities in aqueous solution and in dry storage (see structures in Figure 1). This exceptional stability is a result of their chemical structures; all have electron-donating alkyl groups substituted on the heterocyclic rings adjacent to the oxidative NCI or NBr moieties, which prohibit significant release of "free halogen" into aqueous solution. The combined *N*-halamines thus serve as contact biocides.

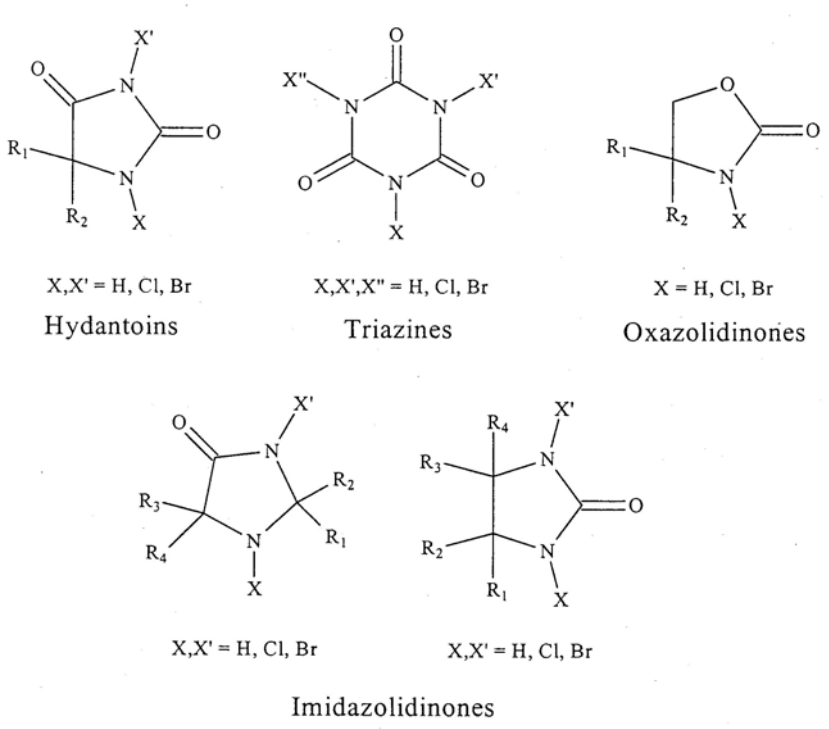

Figure 1: Water-soluble heterocyclic monomers used in modification of polymers to render them biocidal

Although combined *N*-halamine monomers generally require longer contact times at a given halogen concentration than does “free halogen” to inactivate pathogens, it has been demonstrated in these laboratories that it is possible to concentrate *N*-halamine moieties on insoluble polymers, thus producing a substantial reservoir of combined halogen for enhanced disinfection purposes. Furthermore, the functionalized *N*-halamine polymers are superior in overall performance (taking into account biocidal efficacy, stability at varying *p*Hs and in the presence of organic receptors, rechargeability, lack of toxicity, and generally cost) to other biocidal polymers which have been developed and marketed over the years, such as halogenated poly(styrene–divinylbenzene)sulfonamides,[2] polymeric phosphonium materials,[3] and polymeric quaternary ammonium compounds.[4]

Several commercial polymers have been functionalized with *N*-halamine moieties, rendering

them biocidal upon surface contact with pathogens. These include cellulose,[5,6] nylon,[6,7] PET,[6,8] Kraton rubber,[9] various surface coatings,[10] and the *N*-halogenated poly(styrene) hydantoins.[11–15] The latter polymers are granular solids which are insoluble in water and which were packed into glass columns which functioned as a cartridge filters. It was observed that the filters inactivated numerous species of bacteria, fungi, and even rotavirus in only seconds of contact time in flowing water.[11–15] Also, it was observed that the columns did not leach out decomposition products into the water,[14] and that the free chlorine and bromine concentrations leached into the flowing water were less than 0.1 mg/L and less than 2.0 mg/L, respectively. Furthermore, once the halogen supply was exhausted through various loss processes, it could be replenished on the polymers by simply exposing them to flowing aqueous free halogen (*e.g.*, sodium hypochlorite bleach for the chlorinated derivative). It appears that the chlorinated polymer will be useful for potable water disinfection applications throughout the world, and that the brominated polymer will work well in disinfecting recreational water sources. Recently the products have been produced in the form of porous beads to enhance flow properties.

This work represents an extension of technology developed at Auburn University to the preparation of biocidal polyurethane coatings through functionalization of a reactive diol with a hydantoin moiety, which can then be copolymerized with commercial polyols and isocyanates to form the polyurethane. An application of free halogen (*e.g.*, with household bleach) will then render the coating biocidal. The concept is illustrated in Figure 2, and the structure of the actual diol which has been developed in this work is shown in Figure 3.

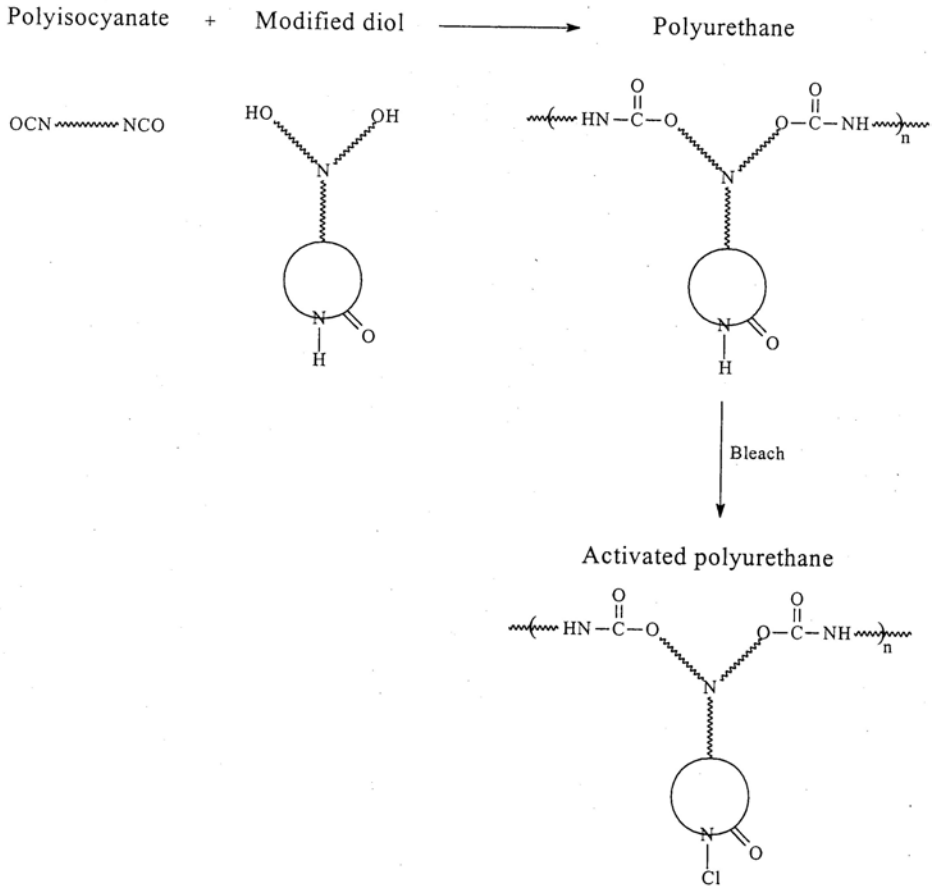

Figure 2: The concept of a biocidal polyurethane coating

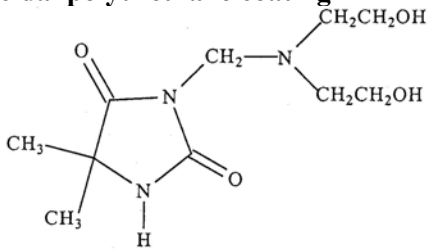

Figure 3: Diol monomer developed for polyurethane coatings

EXPERIMENTAL PROCEDURE

Preparation of Diol Monomer

The unhalogenated diol monomer was prepared by reaction of 132.1 g (1.0 mol) of 5,5-dimethylhydantoin, 106.2 g (1.0 mol) of diethanolamine, and 81.16 g (1.0 mol) of 37% formaldehyde solution in 400 mL of methanol at ambient temperature for 2 h. Alternatively, it could be prepared by reaction of 3-hydroxymethyl-5,5-dimethylhydantoin with diethanolamine in methanol at 75°C. The water byproduct and methanol solvent were removed for characterization purposes by vacuum evaporation. The viscous residue produced was then dissolved in ethyl acetate, and anhydrous sodium sulfate was added for further drying purposes. Following removal of the sodium sulfate by filtration, the solution was refrigerated. After 12 hours, a white solid product precipitated from the ethyl acetate solution. The product, which was removed by filtration from the cold solution, exhibited a melting point of 74–76°C and was produced in 61–84 % yield; it was identified as 5,5-dimethyl-3-(*N*,*N*-di-β-hydroxyethylaminomethyl)hydantoin (see stucture in Figure 3). ^{1}H NMR (DMSO-d_6) δ1.28 (6H), 2.65 (4H), 3.40 (4H), 4.31 (2H), 4.39 (2H), 8.28 (1 H); ^{13}C NMR (DMSO-d_6) δ 24.8, 54.5, 57.6, 57.8, 59.2, 156.2, 178.7; IR (KBr) 1295, 1346, 1439, 1710, 1764, 2814, 2974, 3227, 3474 cm^{-1}.

Preparation and Testing of Polyurethane Coatings

To 10.0 g of commercial waterborne acrylic polyol formulation was added 0.7 g of the unhalogenated diol monomer, prepared as described above, with stirring until dissolution was complete. Then 2.45 g of commercial isocyanate formulation was thoroughly mixed in, followed by the addition and mixing of 2.10 g of distilled, deionized water. The resulting formulation was immediately spread onto the surfaces of several plastic Petri dishes, which were dried in air at ambient temperature. The coatings were dry to the touch within 4–5 h, but were allowed to cure overnight at ambient temperature before further treatment. The coatings were then chlorinated by exposure to commercial bleach (5.25 % sodium hypochlorite) at several concentrations for 3–12 h. After rinsing thoroughly with chlorine-demand-free water, the coatings were dried in air for 6 h and then analyzed for bound oxidative chlorine using an iodometric thiosulfate titration procedure. Other coatings prepared in the same manner at the same time (cut to squares of 6.45 cm^2 area) were challenged with *Staphylococcus aureus* bacteria for contact times of 2 h. This was done by placing 25 μL of bacterial suspension between two coated squares. Following quenching of disinfectant action with 0.02 *N* sodium thiosulfate in a vortexed solution in a beaker, serial dilutions of the vortexed solution were plated onto trypticase soy agar, incubated for 48 h at 37°C, and colony counts were made. Unchlorinated coatings served as controls. The analytical and microbiological evaluations were performed as a function of chlorination concentration and of time following chlorination.

In another experiment, strips of unhalogenated coatings were deposited on the stall doors of a restroom at Tyndall AFB; half of the strips were chlorinated with diluted bleach (20%) with the damp strip being thoroughly rinsed with water after 5 min; the other half were not chlorinated to serve as controls. After 3 months, sterile cotton swabs were used to challenge the strips with 9-μL aliquots of between 10^6 and 10^7 CFU/mL of *Pseudomonas pseudoalcaligenes* JS45, and then again after 6 months without rechlorination. After contact times of 5 min, sterile cotton swabs moistened with sterile buffer were used to recover bacteria from the test sections. The recovered bacteria were inoculated onto trypticase soy agar plates, which were incubated at 30°C for 38 h before colony enumeration.

Finally, polycarbonate strips were coated with the polyurethane and placed in a biofilm reactor at the Center for Biofilm Engineering at Montana State University; uncoated strips served as controls. Water containing nutrients which support biofilm growth was flowed through the reactor at a shear stress simulating a flow of 1 ft/s in a 4-in pipe. After 5 weeks substantial biofilm development had occurred on all strips. At that time the water was doped with 1.0–1.2 mg/L of free chlorine, and the flow was continued for 5 more weeks with the behavior of the biofilms on the strips caused by planktonic bacteria continuously monitored microbiologically.

RESULTS AND DISCUSSION

The data for *S. aureus* inactivation are presented in tables 1 and 2. Table 1 shows that a complete inactivation of the bacteria (>4.5 logs) in 2 h contact time was obtained after 5 and 10 % bleach solutions were used for chlorination for 3 h, and a 3.0-log inactivation occurred following exposure of the coating to 1 % bleach solution for 3 h. This is consistent with the trend of Cl atoms/cm^2 determined analytically for the three types of samples.

Table 1. Biocidal Efficacy as a Function of Chlorination Concentration

Bleach Concentration in Water (%)	Cl Atoms/cm^2 Surface	Log Reduction *S. aureus*
10	1.34 x 1017	>4.5 (no growth)
5	9.13 x 1016	>4.5 (no growth)
1	3.69 x 1016	3.0

[a]Household bleach containing about 5.25% sodium hypochlorite.

Table 2. Coating Chlorine Loadings and Biocidal Efficacies as a Function of Time Following Chlorination with 100 % Bleach for 12 Hours

Time after Chlorination in Days	CI Atoms/cm^2 Surface	Log Reduction S. *aureus*
0.25	3.53 x 1017	>4.7 (no growth)
4.0	6.78 x 1016	>4.7 (no growth)
14.0	2.33 x 1016	>4.7 (no growth)

Table 2 shows that the coatings retained their biocidal efficacies for at least 14 d (longer times were not tested in this particular experiment). It has also been demonstrated that biocidal efficacy can be regenerated once lost by reexposure to free chlorine solutions.

The results of the restroom stall experiment performed at Tyndall AFB were very gratifying. No viable bacteria were recovered from the polyurethane strips which had been chlorinated originally even after 6 months without recharging. Viable bacteria were recovered from the control strips which had not been chlorinated.

Also gratifying were the results of the biofilm reactor study at Montana State University. When the small amounts of free chlorine (1.0–1.2 mg/L) were present in the flowing water, the strips containing the polyurethane coating yielded 1–2 logs fewer biofilm microorganisms than did the polycarbonate strips not containing a polyurethane coating. Figure 4 contains photographs showing the polycarbonate strips with and without the polyurethane coating.

Figure 4: Polycarbonate annular reactor coupons used in the biofilm prevention study; the coupons contain the biocidal polyurethane coating (top) and no coating (bottom).

CONCLUSIONS

A novel hydantoinyl diol monomer has been prepared in a simple, inexpensive process. The monomer has been copolymerized with a commercial waterborne acrylic polyol and a commercial isocyanate to produce a polyurethane coating. The cured coating can be chlorinated with a source of free chlorine, such as household bleach, to render it biocidal. The coating loses its chlorine loading gradually, but it can be regenerated by further exposure to free chlorine. The biocidal coating should have many applications, including in medical facilities, in food preparation areas, in prevention of biofouling, etc.

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